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Recombination processes and luminescence in $Li_6Gd_xY_{1-x}(BO_3)_3$-Eu crystals

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Abstract. The results of investigation of thermally stimulated recombination processes and luminescence in $Li_6Gd_xY_{1-x}(BO_3)_3$-Eu crystals are presented. The steady-state luminescence spectra under X-ray excitation (XRL), the temperature dependence of steady-state luminescence intensity and the thermally stimulated luminescence curves (TSL) were measured at 90-500 K. In the steady-state X-ray luminescence spectra the band at 312 nm related to $^6P_J \rightarrow {}^8S_{7/2}$ transitions in gadolinium ion and bands group at 580-700 nm associated with $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0…4) in Eu^{3+} ion were found to be dominant. The intensity of steady-state XRL of these bands in undoped crystal is increased by 15 times as the temperature changes from 100 to 400 K. The probable mechanisms of temperature dependence of steady-state luminescence intensity and their association with energy transfer of electronic excitations in these crystals are discussed. The investigations have shown the principle complex TSL peak with maximum at 150 K and a number of weaker peaks. The thermal activation parameters (activation energy, pre-exponential factor, kinetic order) for all intense TSL peak have been determined. The origin of small trapping centres caused TSL below room temperature and their association with defects in lithium cation sublattice is discussed.

1. Introduction

Lithium borate crystals with common formula $Li_6(Y,Gd,Eu)(BO_3)_3$ are on careful attention of researchers for a long time not only because their potential applications but by means of solid state physics fundamental investigations too. The main fields of application of these crystals are solid-state detectors and laser devices. They are transparent in a wide spectral range, have high radiation-optical resistance and have a great potential in neutron imaging by scintillation method. Substitution of gadolinium by yttrium essentially decreases the effective atomic number (Z_{eff}) of the compound in the range from 46 to 26, and, consequently, its sensitivity to gamma-background. Utilization of these crystals in laser and scintillation devices implies intense processes of radiation defect formation. However, radiation-induced defects in this crystal have not been studied sufficiently so far. Large amount of publications are devoted to investigations of photoluminescence in visible, ultraviolet and vacuum ultraviolet ranges at 10 and 290 K. Defects and thermally stimulated recombination processes above room temperature were researched in detail by variety of authors. But thermally stimulated recombination processes and recombination luminescence below room temperature was still uninvestigated. While just in that temperature range one must expect revealing of shallow trap centers created by defects in sublattice of weakly bonded lithium cations. Shallow trap centers may affect

strongly the dynamics of electronic excitations and characteristic features of radiation induced defect formation.

The main goal of the present work is a study of thermally stimulated recombination processes and luminescence in lithium borate crystal $Li_6Gd_xY_{1-x}(BO_3)_3$-Eu under X-ray irradiation at 90-500 K.

2. Experimental details

The high optical quality crystals of lithium borates with the general formula $Li_6(Y, Gd, Eu)(BO_3)_3$ were grown at the Institute of Single Crystals NAS of Ukraine, Kharkov. We investigated samples of $Li_6Gd(BO_3)_3$ (LGBO), $Li_6Eu(BO_3)_3$ (LEBO), $Li_6Y_{0.5}Gd_{0.5}(BO_3)_3$-Eu (LYGBO-Eu) and $Li_6Gd(BO_3)_3Eu$ (LGBOEu). Laboratory URS-55 X-ray source with X-ray tube type BSV-2 (Cu-anode, *U*a = 40 kV, *I*a = 15 mA) was used to excite the luminescence. The steady-state X-ray luminescence (XRL) spectra in the range from 1.5 to 6 eV and the temperature dependence of luminescence intensity was recorded using MDR-23 type monochromator (grating 1200 lines per millimeter, the inverse linear dispersion of 1 nm·mm^{-1}) and FEU-106 photomultiplier. FEU-39 was utilized to register curves of thermally stimulated luminescence. All measurements were performed in a vacuum of 10^{-6} Torr. The quick-acting vacuum cryostat with quartz windows was used as the camera for samples and allowed the sample temperature regulating in the range of 80 to 500 K.

3. Results

The X-ray irradiating of the examined crystals leads to steady X-ray luminescence observed at the all temperature range under study. The steady luminescence spectra at 290 K are shown in figure 1. In those spectra characteristic lines of emitting transitions of Gd^{3+} and Eu^{3+} rare-earth trivalent ions dominates. The identification of transitions was completed in terms of Dike's extended diagram. The luminescence at 321 nm corresponds to $^6P_J \rightarrow {}^8S_{7/2}$ transitions in Gd^{3+} ion, the group of lines at 580-700 nm is related to $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0…4) in Eu^{3+} ion.

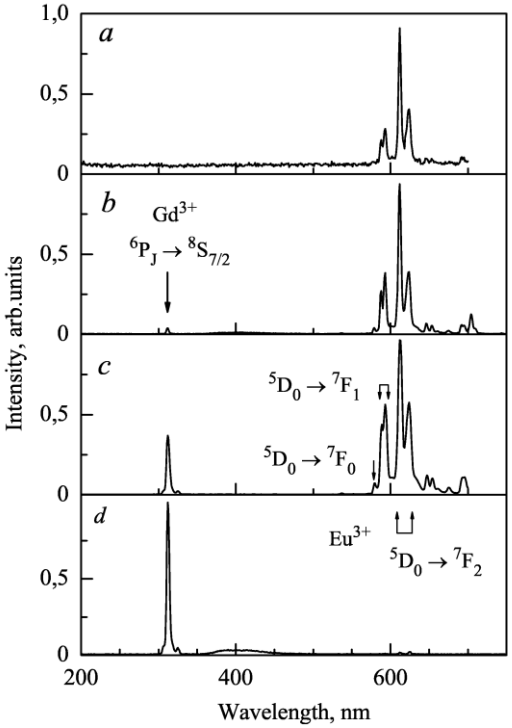

Figure 1. Steady-state XRL spectra of LEBO - (a), LGBO-Eu - (b), LYGBO-Eu - (c) and LGBO - (d) at 290 K.

Temperature variations in the examined range do not lead to principal changes in steady-state X-ray luminescence – only lines intensity are changed. Temperature dependence of steady-state

luminescence intensity of the examined crystals is shown in figure 2. It is seen that temperature increasing from 100 to 400 K leads to intensity increasing by 15 times (from I_L.to I_H). In coordinates (Y = ln(I_H/I-1), X = 1) this experimental data approximates well by linear dependence. In this case it is possible to describe the temperature dependence of steady-state luminescence with the formula:

$$I(T) = I_0 + \frac{I_m}{1 + W \cdot \exp(-B \cdot T)}, \quad (1)$$

where I_0, I_m, W and B – parameters of approximation. The constant element I_0 is utilized for better convergence.

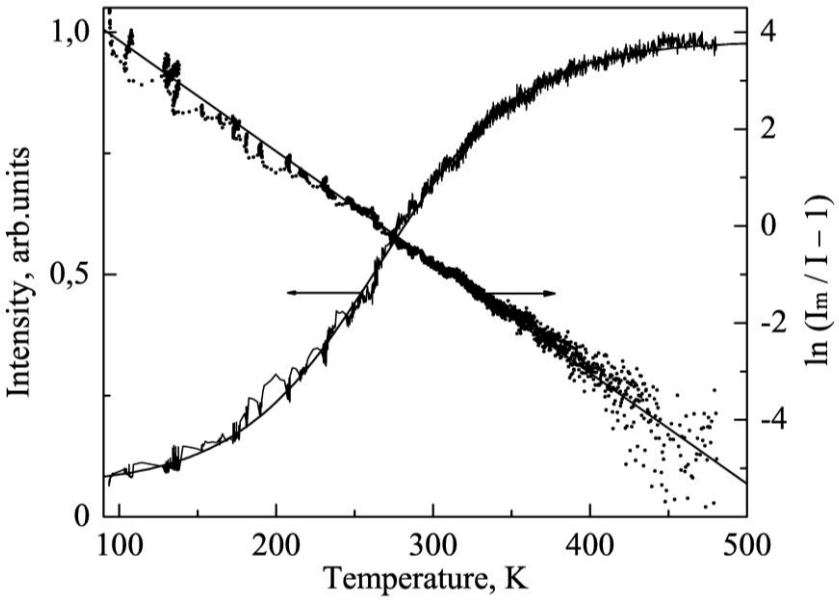

Figure 2. Temperature dependence of the intensity of the steady-state XRL of crystal LGBO in the band at 312 nm, presented in two different coordinate systems. The solid smooth lines - the result of the approximation.

Temperature dependence of the intensities of the steady-state XRL at λ_m = 613 and 312 nm for the LEBO and LYGBO-Eu crystals were also measured. They were qualitatively similar to those for LGBO, so the figures are not included. The table 1 shows the parameters of temperature dependences of the steady-state XRL approximation with formula (1) for LGBO, LEBO, LYGBO-Eu crystals.

Table 1. Parameters of approximation of the temperature dependences of steady-state XRL.

Parameter	Crystal			
	LGBO	LEBO	LYGBO-Eu	
λ_m, nm	312	613	312	613
I_H/I_L	14.7	15.1	2.9	1.8
$100 \cdot I_0/I_H$	6.6	5.7	32	57
ln$W$	5.86	4.56	3.59	6.46
$100 \cdot B$	2.2	1.3	1.7	3.6

Figure 3 and figure 4 show the curves of thermally stimulated luminescence of Li_6(Y, Gd, Eu)$(BO_3)_3$ measured at the linear heating rate of 0.3 K·s^{-1} after irradiation by X-rays at 90 K. To approximate the TSL peaks we used the three-parameter model of the general order kinetics. In the framework of the OTOR (One trap, one recombination) for each peak of the TSL in the approximation of experimental data thermal activation parameters were obtained: activation energy E, pre-

exponential factor *S* and the kinetic order *p*. In table 2 for the most intense TSL peaks thermal activation parameters, the temperature position of the maximum and relative intensities are displayed. We would like to note that after the irradiation at 90 K the strong afterglow was observed, and its intensity in some cases reached 10-15% of the maximum intensity of the TSL. The presence of the afterglow was taken into account when the experimental data was processed by using the definition of the formal TSL peak with temperature just below the temperature of irradiation.

The characteristic feature for all crystals studied is the presence of the complex TSL peak at 110-170 K. The results of the approximation of the TSL peak (figure 3, figure 4 and table 2) indicate the presence in its composition from one to three elementary TSL peaks, the composition and structure of which varies a little from crystal to crystal. Thus, the main TSL peak for the LGBO crystal is located at 140 K and consists of two elementary peaks at 138 and 148 K (table 2). In addition to the TSL curve in LGBO we observed two less intense peaks at 279 and 313 K and the weak expression of TSL at 230 K, figure 3.

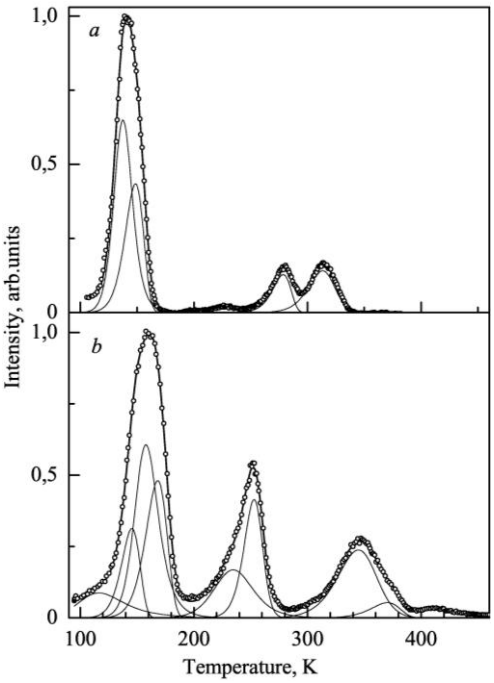

Figure 3. LGBO TSL curves - (a), LYGBO-Eu - (b), measured at a linear heating rate of 0.3 $K \cdot s^{-1}$ after irradiation by X-rays at 90 K. The circles are the experimental data, solid lines - the result of approximation.

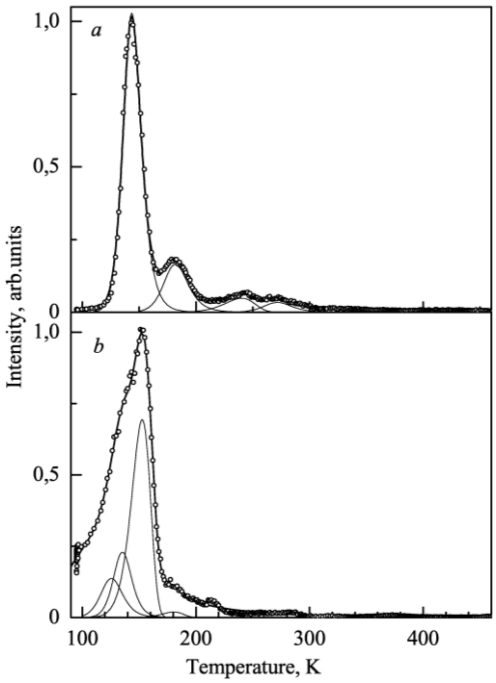

Figure 4. LEBO TSL curves - (a), LGBO-Eu - (b), measured at a linear heating rate of 0.3 $K \cdot s^{-1}$ after irradiation by X-rays at 90 K. The circles are the experimental data, solid lines - the result of approximation.

In the LGBO-Eu crystal the main non-elementary TSL peak is observed at 151 K, figure 4. It consists of three elementary peaks at 126, 136 and 152 K, table 2.

In the LEBO crystal the main TSL peak at 143 K can be described by a single elementary component, table 2. Also the far less intense peak at 188 K and the weak expression of TSL at 180-250 K are observed, figure 4.

The most structured TSL curve is obtained for the LYGBO-Eu crystal, figure 3. In this crystal the principal complex TSL peak is located at 158 K and consists of three elementary TSL peaks at 145, 158 and 168 K. In addition two more intense non-elementary TSL peaks are observed at 252 and 347 K, which are characteristic only for LYGBO-Eu, figure 3.

Table 2. Parameters of TSL curves approximation.

Crystal	T_m, K	E, eV	S, MHz	p	I_m, a.u.
LYGBO–Eu	145	0.22	1.4	1	31.3
	158	0.28	39	2	60.9
	168	0.25	1	1	48.3
	234	0.36	1	1.8	16.8
	253	0.77	$7.9\cdot10^7$	1.3	41.5
	346	0.67	100	1.3	23.6
LEBO	143	0.31	3800	2	100
	188	0.37	810	2	18.3
LGBO	137	0.26	190	1.8	64.9
	148	0.23	1.8	1	43.5
	279	0.84	$5.3\cdot10^7$	1	12.8
	313	0.82	$5.1\cdot10^5$	1.3	14
LGBO–Eu	126	0.26	160	1.8	13.5
	136	0.18	0.7	1.8	22.5
	152	0.24	1.9	1	68.6

Note. Tm - temperature of the maximum peak of TSL; I_m – intensity of elementary TSL peak as a percentage of the maximum intensity in the examined temperature range; E - activation energy; S - pre-exponential factor.

4. Discussion

All known data about lithium borates $Li_6(Y, Gd, Eu)(BO_3)_3$ crystals indicate the significant similarity in terms of crystal structure, the dynamics of electronic excitations and thermally stimulated recombination processes. In [1, 2] it has been found that the intrinsic luminescence of undoped LGBO is due to the radiative transitions $^6P_J \rightarrow {}^8S_{7/2}$ in the Gd^{3+}matrix ion. At temperatures above 40 K the main mechanism of electronic excitations energy transfer in LGBO is rapid diffusion of electronic excitations between the neighboring Gd^{3+}ions in the one-dimensional chain [$\cdots Gd^{3+}– Gd^{3+}–Gd^{3+}\cdots$]. This is due to the crystallographic structural features of LGBO: distance $Gd^{3+} – Gd^{3+}$ in the chain is 0.388 nm, and the one between the chains – 0.665 nm [3, 7, 8]. It has been established experimentally [11] that in the LGBO crystals, the limiting distance R_c for energy transfer between Gd^{3+} ions on the mechanism of the exchange interaction is R_c = 0.5 nm, and if in addition to the exchange interaction is further realized by dipole-dipole interaction, then R_c = 0.65 nm. The distance between neighboring chains of Gd^{3+} ions slightly exceeds this value, therefore, at temperatures above 40 K the energy migration of electronic excitations on the chains of gadolinium ions is dominated. The one-dimensional energy migration prevents concentration quenching of the intrinsic fluorescence of Gd^{3+}matrix ions [3].

The yield of luminescence at 312 nm in LGBO determined mainly by two competing processes: the radiative transitions in Gd^{3+} with probability ω_1 and the transfer of electronic excitation energy between neighboring ions Gd^{3+} with probability ω_2

$$\eta(T) = \frac{I(T)}{I_H} \approx \frac{\omega_1}{\omega_1 + \omega_2}. \quad (2)$$

In LGBO the temperature dependence of the steady-state XRL intensity $I(T)$ can be attributed to the change in the ratio between the probabilities of these two processes under temperature changing. However, the alleged reasons for this change can be different. We would like to discuss some of them.

One of the possible reasons is the thermal expansion of the crystal, which determines the temperature dependence of the distance between neighboring ions in the chain

$$r(T) = r_0 \cdot (1 + \alpha \cdot (T - T_0)), \quad (3)$$

where r_0 – the distance between the ions at a temperature T_0, α – the coefficient of linear thermal expansion of the crystal along the chain of gadolinium ions. In case of the exchange interaction

$$\omega_2 = \omega_{20} \cdot \exp\left(-\frac{r}{a}\right), \tag{4}$$

where ω_{20} – pre-exponential factor, a – half the Bohr radius, r – the distance between neighboring ions Gd^{3+} in the chain. Substituting $r(T)$ in (4), from (2) we obtain

$$\eta(T) = \frac{1}{1 + W \cdot \exp(-B \cdot (T - T_0))}, \tag{5}$$

where W – the constant, $B = \alpha(T) \cdot r_0/a$. The resulting expression is quite comparable with the empirical relation (1) found by us.

In the case of dipole-dipole interaction

$$\omega_2 = \frac{C}{r^6}, \tag{6}$$

where C – constant. Substituting into (2), we obtain

$$\eta(T) = \frac{1}{1 + (C \cdot r_0^{-6} / \omega_1) \cdot (1 + \alpha \cdot (T - T_0))^{-6}}, \tag{7}$$

In the coordinates ($Y = \ln(I_H/I - 1)$, $X = T$) this dependence is quite satisfactorily approximated by a straight line $Y = A - B \cdot T$ with a slope $B \approx 6\alpha$.

Despite of the fact that the qualitative temperature dependence of the stationary XRL intensity can be attributed to thermal expansion of the crystal, the quantitative estimate of the parameter B in both cases is approximately two orders of magnitude below the experimentally observed values of B, table 1.

Another reason could be the temperature dependence of the probability of ω_1. Indeed, most low-energy excited levels of the ion Gd^{3+} caused by ^6P_J conditions. These radiative transitions from these states to the ground state $^8S_{7/2}$ cause the observed luminescence at 312 nm. Excited levels ^6I located at $\Delta E \approx 300$ meV higher in energy than ^6P_J. It is known [1] that in LGBO vibrational energy relaxation between the ^6I and ^6P_J is non-radiative. At the same time the migration of electronic excitation energy of levels in the ^6I chains in Gd^{3+} ions is more efficient than the ^6P_J levels. Assuming that the probability ω_1 is limited by the rate of vibrational relaxation $^6I \rightarrow {}^6P_J$, we write

$$\omega_1(T) = \omega_0 \cdot (n + 1)^p, \tag{8}$$

where p – process order (the number of phonons with energy $\hbar\omega$), necessary for covering the energy interval $\Delta E = p \cdot \hbar\omega$), n - the number of phonons with the given energy, ω_0 - the likelihood of the process at zero temperature. In the thermodynamic equilibrium the average number of phonons at a given level of $\hbar\omega$ estimated by the formula

$$\langle n \rangle = \frac{1}{\exp(\hbar\omega / k_b T) - 1}, \tag{9}$$

where k_b - Boltzmann constant. It is easy to see that

$$\omega_1(T) = \frac{\omega_0}{\left[1 - \exp(-\hbar\omega / k_b T)\right]^p}, \tag{10}$$

$$\ln(I_H / I - 1) = \ln(\omega_2 / \omega_0) + p \cdot \ln(1 - \exp(-\hbar\omega / k_b T)). \quad (11)$$

In the temperature range 100-500 K this dependence for reasonable values of parameters allows a good quantitative agreement approximated the experimental data on temperature dependence of the steady-state XRL intensity.

The presence of small crystal trapping centers may also lead to the steady-state XRL intensity "buildup". We would like to discuss the known data concerned the lattice defects of lithium borates.

The intrinsic defects in the lithium sub-lattice is currently the most studied for lithium triborate LiB_3O_5 (LBO). Irradiation by X-rays at 80 K leads to the formation of several types of electron and hole trapping centers. Electron paramagnetic resonance (EPR) and nuclear magnetic resonance identified several types of the trapped-hole centers with a generalized name - points of O^- type [5-7]. Center O^- represents a hole trapped at 2*p*-orbitals of oxygen ions located at the junction of the two structures BO_3 and BO_4, with a substantial delocalization of electron density in the direction of p_z-orbital of boron atom. Different types of the trapped-hole centers of O^- type in LBO differ only by the way to stabilize a localized hole on the oxygen ion.

A hole center of *A*-type is formed when a hole stabilized by the tetrahedral structure BO_4, slightly distorted as a result of the lattice relaxation after the capture of a hole [8]. This center can be compared with self-localized hole. The thermal stability of *A*-center is limited to a temperature of 130 K [5, 6].

A *B*-type hole center is formed when a hole is stabilized on the oxygen ion by negative charge of the lithium vacancy in the first coordination sphere. *B*-center thermal stability reaches 200 K [8].

An electronic B^{2+} center in LBO crystal was found and identified by ESR after irradiation by X-rays at 80 K [5]. Based on these experimental data and calculation results [9] the most adequate model of the center is that of an interstitial boron atom with additional captured electron. The center B^{2+} in the crystal LBO is thermally stable up to 170 K.

The trapped-hole centers are also visible in the spectrum of low-temperature induced optical absorption of LBO [10]. The thermal fading curves are comparable with the temperature dependence of non-isothermal relaxation of paramagnetic centers and the O^- and B^{2+} [5] and are characterized by two stages of color centers annealing: at the 130 K and near 200 K [10]. In these temperature ranges we found intense LBO TSL peaks, the main ones of which are located at 130 and 240 K.

Earlier in the LGBO crystals at room temperature were also found short-lived antimorphic defects of the lithium sublattice, causing metastable optical absorption of these crystals after pulsed irradiation [4]. Measured in [4] the parameters of the temperature dependence of the decay kinetics of the metastable optical absorption amounted to E = 0.32 eV and $\omega_0 = 4 \times 10^5$. Thermal activation parameters of the TSL peaks in LGBO obtained in this work, (table 2) are close to these values, so the main low-temperature TSL peaks at 120-160 K, typical of all crystals of lithium borates, appropriately referred to the intrinsic defects of the lithium sub-lattice.

A lithium vacancy may be formed not only by radiation exposure, but also in the process of growing crystals to compensate for the excess of heterovalent impurities electric charge or any structural defects of the lattice. Capturing a hole in 2*p*-orbital of the oxygen ion on irradiation by X-rays leads to the formation of a hole center of O^- type. Impurities or structural defects in the vicinity of the center affect only the energy depth of the hole-trapping center, and the specificity of the impurity or structural defects in most cases, show no appreciable effect. In all cases we say about centers of O^- type. This explains the observed similarities and differences in the pattern TSL various lithium borates. Significant influence of the dopant was observed only for LYGBO-Eu, figure 3. In this compound, ions of yttrium substitute for gadolinium [2], which leads to dilution of the chain of Gd^{3+} ions, which is the energy transport of electronic excitations. This explains both the appearance of additional trapping centers associated with the presence of yttrium ions in the lattice, and a sharp reduction of the effect of "buildup" of the stationary XRL intensity in LYGBO-Eu, table 1.

Comparison of the temperature dependence of the RL intensity (figure 2, table. 1) with the curves of TSL (figure 3, figure 4, table 2) indicates that the maximum of "buildup" of the XRL intensity does not correlate with the position of the TSL intensity peaks. At the same time, in the LBO crystals the

maximum "buildup" of the steady-state XRL intensity, due to the presence of small crystal trapping centers, coincides with the temperature position of the most intense TSL peak hole. This suggests that the mechanism of "buildup" of the steady-state XRL intensity in the crystals $Li_6(Y, Gd, Eu)(BO_3)_3$ has a different nature and is not related to the presence of small trapping centers in these crystals.

5. Conclusion

Based on the results of thermally stimulated recombination processes and the luminescence of $Li_6Gd(BO_3)_3$, $Li_6Eu(BO_3)_3$, $Li_6Y_{0.5}Gd_{0.5}(BO_3)_3$-Eu and $Li_6Gd(BO_3)_3$-Eu in the temperature range 90-500 K revealed that the spectra of steady-state RL of these crystals is dominated by the band at 312 nm, corresponding to the $^6P_J \rightarrow {}^8S_{7/2}$ transitions in Gd_{3+} ion and the group of lines at 580-700 nm, due to the $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0... 4) in Eu^{3+} ion.

The intensity of the steady-state RL in these bands increases by several times when the temperature changes from 100 to 400 K. Analysis of possible mechanisms of the observed temperature dependence of the steady-state RL intensity revealed their connection with the peculiarities of energy transfer of electronic excitations in these crystals. The most probable reason of the steady-state XRL intensity "buildup" is the competition between the temperature dependence of vibrational energy relaxation of electronic excitations between the ^6I and ^6P_J states and the process of rapid diffusion of electronic excitations on neighboring ^6I states in the chain of Gd^{3+} ions.

The main non-elementary TSL peak with the observed maximum at 110-160 K in all crystals of lithium borates is assigned to a defect of lithium cations sub-lattice. The impurities or structural defects in the vicinity of these centers may affect the depth of its energy, causing the observed diversity of small capture centers of the O^- type. At the same time, any properties of impurity or structural defect in most cases do not significantly affect the specificity of shallow trapping centers.

Doping of lithium borate by yttrium ions not only leads to the decreasing of the crystal effective atomic number, but also sharply reduces the temperature dependence of steady-state XRL and causes the appearance of two intense peaks of TSL at 252 and 347 K. In LYGBO-Eu crystal yttrium ions substitute gadolinium ions [2] in the chains along which the transport of energy electronic excitations occur. Yttrium ions block the flow of energy in the chain, and it is a possible reason of the additional trapping centers. According to the above conclusions the observed temperature dependence of the stationary XRL intensity is due to competition between the energy relaxation on the Gd^{3+} ion and the migration of energy along a chain of Gd^{3+} ions. Lowering the probability of energy migration along a chain of Gd^{3+} ions in the LYGBO-Eu compound should reduce the temperature dependence of the stationary XRL intensity. This is the result observed in our experiments, table 1.

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